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Message:

Transmitted herewith is an English translation of the Abdel-Reihim reference which you cited in the last office action of application S.N. 09/579,531

Abdel-Reihim, Metall, 38. Jahrgang, Heft 5, Mai 1984

(English title: Strengthening of Pb-Sb and Pb-Ca alloys through deformation)
Microstructure and Mechanical Properties of Pb-Alloys for Use in Expanded Grids after Deformation and Recrystallization.

(English Abstract: Strengthening of Pb-Sb and Pb-Ca alloys through deformation. Investigation of the effect of alloying content and addition, microstructure and deformation on strengthening of Pb-Sb and Sb-Ca alloys)

In light of requirements associated with manufacturing of expanded metal grids for batteries the deformation behavior of Pb-<1.5% Sb alloys with the addition of Te, As, Cu, Cu+As+Ag was investigated. In addition PbCa0.08 and PbCa0.08Sn1.0 alloys were investigated. One consideration was the influence of various grain structures achieved by varying the cooling conditions.

1. Introduction:

Lead-acid battery grids are typically manufactured using casting processes. These conventional processes do have some technical problems including the setting and maintenance of favorable kettle and mold temperatures and pressures that are important for the mold-filling behavior, hot-cracking and grid porosity. They do provide the battery producer with the advantage of providing great flexibility to manufacture a great variety of grid types as well as small series production capabilities. Even when considering the cost, the higher oxidation losses and the elaborate environmental requirements, grid-casting processes remain competitive with grid expansion processes.

The grid casting process was initially replaced by expansion processes in the USA, while in Europe casting processes still dominate. In Europe, too, the expansion process should be considered. The advantages of expansion processes [1, 2] include a reduction in the cost of energy by 60%, higher throughputs, a reduction in the material use by 15%, less stringent environmental protection measures - which is of particular importance at present - and substantially reduced labor cost.

The starting point is a cast slab that is rolled in one or several steps to a strip thickness of about 1.2mm. The strip is slit by a punch and subsequently expanded to the desired grid geometry. During this process the article experiences deformations of various degrees resulting in hardening effects that are negatively affected by the occurrence of softening and recrystallization processes as the recrystallization temperatures are below room temperature.

Investigations performed to date [2-7] deal with Pb-Sb alloys with Sb content of 2-20%. Alloys with low-Sb content (<1.5%) or Ca substituted for Sb, as they are currently used in low-maintenance batteries [8], have not been investigated so far. In addition to the electrical and chemical property requirements, there are minimum mechanical properties (HV>12) required in the production process. Heretofore, Sb contents >2.5% were required. A reduction of these minimum concentrations requires an enhancement of the mechanical properties to improve processibility. Additives were sought and found to

harden the materials (Ag, As) for use in cast alloys. A further enhancement of the mechanical properties was achieved [8] using grain-refining additives. In this case Se, particularly selenides (Ag_2Se) have been used satisfactorily. The grain refining properties of PbSb alloys improved the hot cracking, the material flow as well as hardness of cast grids and their age-hardening properties. Substitution of Sb with Ca or Ca-Sn increased the hardness due to mixed grain precipitation and due to their tendency to precipitate. The properties of expanded grids are controlled by melt chemistry, the primary grain structure and the secondary structure influenced by the rolling deformation and the expansion process.

The present investigation deals with variation of the alloy composition and the cooling conditions as well as the degree of deformation.

2. Experimental:

Starting alloys, listed in table 1, include PbSb1.5 and PbCa0.13. The Ca content of 0.13% accounts for the Ca loss experienced during remelting and in the holding furnace. The cast alloys contained a maximum Ca content of 0.08%.

The melting temperature set at the furnace, containing the alloys in a steel crucible, was 500°C, melt time was 20 minutes minimum and the melt mass was 0.35kg. The material was cast into uncooled steel molds with the dimensions 27x10x90mm.

To vary the cooling temperature part of the samples were cast into forms placed in the oven that was then turned off to obtain a slow cooling rate.

To determine the effect of alloying or impurities, additions of As, As+Cu, Bi, Ag, Cu (in the form of SbCu_{12}), Te and Se as grain refiner was added according to table 2 to the starting alloy of PbSb1.5. In addition, the Sb content was varied and 0, 0.1, 0.3, 0.5 and 1.5% Sb containing alloys based on technical grade Pb (99.98%) were prepared.

In addition to PbCa0.08 a PbCa0.08Sn1 alloy was investigated. The cast alloys were rolled in seven steps using a four-step rolling mill system to a total deformation of 90%. After each rolling steps samples were taken for optical microscopy and hardness measurements. Hardness was determined using the Vickers scale with a load of 1kg and duration of 3 minutes. To exclude the influence of microstructure changes (age hardening or recrystallization) the measurements were always performed two days after rolling.

3. Results

3.1 Deformation hardening of PbSb alloys

- Influence of addition of As, Bi, Ag, Cu, Te.

Figure 1 shows the hardness as a function of the degree of deformation for the starting alloy, the starting alloy with 0.05% As, and the starting alloy with 0.05% As and 0.05% Cu. Irrespective of the additives the hardness increases up to 30% deformation and then drops back to the initial value at about $\eta=75\%$, it remains stable after up to $\eta=90\%$. The

effect of increasing Bi content on the hardness is displayed in Figure 2. Increasing the Bi content changes the maximum hardness depending on content and deformation and at 0.05%Bi a hardness increase of 30% is observed. When increasing the Bi content to 0.3% a smaller hardness increase (about 10%) is observed and the maximum is clearly shifted to lower degrees of deformation.

Ag additions (Figure 3) result in a similar hardness behavior as a function of the deformation; however, merely 0.1%Ag addition results in an increase of the maximum hardness by 50% at $\eta=30\%$.

The effect of the Ag addition diminishes with increasing degrees of deformation and is no longer present at $\eta=50\%$. The microstructure for $\eta=30\%$ and 80% of an alloy containing 0.1%Ag is shown in Figure 4 a and b. The degree of recrystallization increases with increasing level of deformation, whereas the grain size decreases – as is well known.

Figure 5 shows the age hardening of an SbSb1.5 alloy with and without Cu additions. Up to a deformation level of 20% the amount of Cu has no effect on the hardness. Between 20 and 75% deformation the addition of Cu results in apparent reduction hardness. Above 75% deformation the hardness is reduced only marginally. The Cu content is of insignificant importance, although higher Cu additions (0.15%) reduce the hardness up to a deformation of 75%. Above 75% this influence is reversed.

Te additions (figure 6) hardly affect the hardening behavior and are comparable to As additions (Figure 1).

- Effect of Sb (0 to 1.5%)

Figure 7 illustrates the hardness behavior as a function of the Sb content. It is apparent that at As levels of $<0.3\%$ no hardening effect is observed. The hardness remains constant at about 4 HV. Higher Sb additions (0.4-1.5%) result in a drastic hardness increase to HV 8, followed by further hardening up to 30% deformation. Thereafter the hardness decreases continuously to a final value of HV 7. The maximum hardness is typically reached at $\eta=30\%$, the value is proportional to the Sb content.

3.2. Deformation hardening of PbCa alloys

- Effect of additives (1% Sn) and cooling rate

Figure 8 clearly indicates that the hardening behavior of PbCa0.13 alloys depends on the cooling rate (oven/air) during casting. Slowly cooled samples show no hardness increase as a function of the deformation. Starting and final hardness after 80% deformation remains the same at HV 7.

Rapid cooling (air) increases the initial hardness drastically to 11 HV. It can be further increased by the following deformation to 12 HV (between $\eta=15\%$ and 55%) and drops following deformation by 80% to HV 7 to the same value of the oven-cooled sample. A Sn addition of 1% as typical in battery grids does not significantly influence this behavior; however, between $\eta=15$ and 55% maximum hardness values of HV 16 are

observed: at degrees of deformation exceeding 80% the hardness remains independent of the Sn addition.

- Effect of the structure development on the deformation hardening of PbSb and PbCa alloys

To determine the influence of the structure on the deformation hardening of PbSb and PbCa alloys samples were solidified using different cooling rates. The resulting structure is indicated in Figure 9a and b. As expected, the grain size increases with reduced cooling rate. The addition of 0.01 % Ag₂Se significantly effects the grains size (Figure 9c). Grain refinement results in rounded, rosettes-like fine dendrites – and an almost spherical structure.

The resulting deformation hardness behavior is displayed in figure 10. In contrast to the various initial hardness of PbCa alloys (compare with figure 8), the initial hardness of PbSb alloys remains the same; however, the refinement of Ag₂Se results in a significant hardness increase.

The hardness behavior remains the same regardless of the process, with the exception of oven-cooled PbCa alloys. The reason why oven-cooled PbSb alloys achieve a hardness maximum at 40% deformation, can be explained by the hindrance of the recrystallization due to Sb precipitation. In general it is observed that with decreasing initial grain sizes the maximum hardness is shifted to lower deformation values.

Independent of the alloy composition and the process all samples, after high degrees of deformation (>80%), show a similar hardness of 7 HV.

This can be explained by the similarities in the grain structures (Figure 11a and b).

4. Discussion

In this study the influence of various parameters (structure formation, alloy composition, additives) on the hardening behavior of Pb alloys was investigated.

The results show an initial drastic hardness increase of cast samples for Sb contents of 0.3% and 0.5%. The hardness increase is related to the structure formation. The structure obtained when solidifying low Sb level alloys is cellular with increased Sb levels at grain boundaries and becomes dendritic with increased Sb contents. In this case Sb is located in the solidified eutectic melt regions (Figure 9b). The transition in the structures is not observed at a fixed Sb content, as it is furthermore influenced by the cooling rate and therefore the solidification rate [9].

Cellular formed structures (in this case 0.3% Sb) have as cast hardnesses about 40% lower than dendritic solidified structures (in this case at or above 0.5% Sb).

Differences in the structure furthermore influence the subsequent deformation (figure 7). Recrystallization of cellular structures is observed after low degrees of deformation and consequently no hardening effect is observed. Hardness is largely independent of the

degree of deformation. Dendritic solidified structures experience a noticeable hardness increase with increasing Sb content (in this case $>0.5\% \text{Sb}$) and therefore increasing eutectic structure components in lower deformation ranges ($\eta < 50\%$). 1.5% Sb has a hardness maximum of 50% and is observed at 30% deformation. This hardness values remain even after prolonged storage times. The cause is that the inhomogeneously-deformed structure only partially recrystallizes during the deformation process (according to Figure 4a) and the resulting hardness is determined by the volume ratio between recrystallized (low hardness) and unrecrystallized (high hardness) structure. With increasing degree of deformation and therefore increased degree of recrystallization and increased dispersion of the Sb the hardness drops to a value similar to the one of the as cast materials, as the grain boundary effect diminishes, despite homogeneous distribution of the particles in the matrix - due to their size and distance - and no compensating dispersion-hardening effect is achieved.

The reasons for the different influence of As, Te and Cu/As (no effect) as well as Cu by itself, all of which are soluble in Pb and form mixed grains (reduction of hardness) is subject to additional investigations. Ag additions, which predominantly precipitate near grain boundaries, however, similar to Sb itself, result in an increase in hardness (Figure 3) with a maximum of almost 100%.

Oven cooled PbCa0.13 alloys (figure 8) show typical as cast hardness in Pb alloys of HV 7. Ca is mainly present in Pb₃Ca precipitates. Therefore no age hardening is observed. With increasing cooling rate (air), over saturation and precipitation hardening occurs, increasing the as-cast hardness by 60%. Sn additions have no effect. Subsequent deformation enhances the hardening process and, in conjunction with recrystallization, result in a further hardness increase, which is retained up to about 60% deformation. Adding the common 1%Sn, as explained above, a hardness increase of 30% is observed due to the precipitation of Pb_xSn_y-Ca + Sn₃Ca. Overaging and the resulting increased recrystallization reduces the hardness at degrees of deformation of over 60% and, at 80% deformation, achieves a hardness value equivalent to the oven-cooled alloy of HV 7. The results further indicate, in agreement with alloys of 2.1 to 15.6 Sb [3], that at degrees of deformation exceeding 80% of all alloys investigated the hardness remains similar for all samples (HV 7); except for Pb alloys with Sb contents below 0.5%, which match the hardness of unalloyed Pb (HV 4).

These results are important considerations for grids produced using expansion processes.

In summary it is emphasized that the grain size is more important for the hardness behavior than the size of cellular dendrites. Grain refined Pb-Sb alloys already soften after 20% deformation (Figure 10) due to recrystallization, in not grain-refined alloys and PbCa alloys it occurs after about 50%. In this case hardness and deformation properties have to be distinguished. The orientation of the dendritic grain is critical for the deformation - and not the size of the cells that it is formed from. Due to the local restrictions however, these cells control the measured hardness values.

Table 1: Composition of the starting alloys

Table 2: Additives added to the starting alloy (table 1)

Figure 1: Effect of As additions (also combined with Cu) to PbSb1.5 on the hardness and deformation

Figures 2: Effect of Bi additions to PbSb1.5 on the hardness and deformation

Figures 3: Effect of Ag additions to PbSb1.5 on the hardness and deformation

Figures 4. Structure development (V= 50:1)

- a) PbSb1.5Ag0.1 (30% deformation)
- b) PbSb1.5Ag0.1 (80% deformation)

Figure 5: Effect of Cu additions to PbSb1.5 on the hardness and deformation

Figures 6: Effect of Te additions to PbSb1.5 on the hardness and deformation

Figures 7: Effect of Sb content of PbSb alloys on the hardness and deformation

Figures 8: Effect of Sn content and the cooling rate on the hardness and deformation of PbCa0.13

Figures 9. Structure development (starting material) V= 50:1

- a) PbSb1.5 (air cooled)
- b) PbSb1.5 (oven cooled)
- c) PbSb1.5 (grain refined with Ag2Se)

Figures 10: Effect of structure development on the hardness and deformation of PbSb1.5 and PbCa0.13

Figures 11. Structure development after 80% deformation (V= 100:1)

- a) PbCa0.13 (air cooled)
- b) PbSb1.5 (air cooled)